

KINETICS OF DEUTERIUM EXCHANGE OF RESORCINOL IN D₂O AT HIGH PRESSURE AND HIGH TEMPERATURE

Clement R. Yonker, Shi Bai, and Bruce J. Palmer, Environmental and Energy Sciences
Division, Pacific Northwest National Laboratory, Richland WA, 99352

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ABSTRACT

The exchange kinetics of deuteration of resorcinol in pure D₂O were studied using a flow-through capillary tubular reactor with *on-line*, proton and deuterium NMR detection at high temperatures and high pressure. The temperatures of these measurements covered a range up to 450°C at a pressure of 400 bar. The hydrogen/deuterium (H/D) exchange in resorcinol (1,3-dihydroxybenzene) under these extreme conditions was easily detected by both proton and deuterium NMR as a function of resorcinol residence time in the capillary tubular reactor, which also served as the high pressure NMR cell. The qualitative NMR results indicate that H/D exchange in resorcinol is observed at 200°C. The kinetics of H/D exchange in resorcinol and the activation energies were extracted from the experimental ¹H and ²H NMR data.

INTRODUCTION

In subcritical (superheated) and supercritical water the hydrothermal oxidation of many organic compounds are enhanced due to the increased reactivity of the substrate and the enhanced solubility of non-polar organic compounds at these high temperatures. The increased reactivity of organic compounds in superheated water has been recognized for its potential in the destruction of toxic and organic wastes via oxidation.^{1,2}

Hydrogen/deuterium (H/D) exchange of some extremely weak organic acids in supercritical water has been investigated.^{3,4} Yao and Evilia³ estimated the equilibrium constant for the acid-base reaction of H/D exchange of benzene with OD⁺ to be three orders of magnitude higher at 400°C than at 25°C. Qualitatively, for substituted benzene compounds (fluorobenzene, 1,2-diphenylhydrazine, and nitrobenzene), the hydrogen in the ortho position was found to be slightly more acidic than those in the para or meta positions when reacted under basic conditions in D₂O at 400°C.³ However, difficulties were encountered when attempting to obtain quantitative chemical kinetic data for these reactions due to the large experimental error in determining temperature, pressure, and heating time when using a batch reactor.

While, NMR has not been widely used for *in situ* investigations of reactions in supercritical water, it has been used to monitor batch reaction products after quenching. The use of NMR detection for the *in situ* study of chemical kinetics generally requires that the NMR data acquisition time for a spectrum be much shorter than the reaction half-life.⁵ An experimental effort using a high pressure, high temperature flow-through capillary tubular reactor with *on-line* NMR detection for the investigation of H/D exchange of resorcinol in superheated and supercritical water will be discussed. The pseudo-first order rate constant for H/D exchange was determined by the disappearance of the α -hydrogens in resorcinol for the first time under these extreme conditions using this micro-volume ¹H NMR technique. In a similar manner, the product of the H/D exchange reaction was monitored *on-line* by ²H NMR. The rates for the resorcinol hydrogen/deuterium exchange reaction and the difference in the reactivity of the α and β hydrogens on resorcinol will be described.

EXPERIMENTAL

Resorcinol (Aldrich Chemical Company, Inc.) was used without further purification. To deoxygenate the solution, D₂O (Cambridge Isotope Laboratories) was boiled for 5 minutes under dry nitrogen and a 20% (w/w) resorcinol-D₂O solution was prepared and purged using dry nitrogen for 10 minutes.

Flow-through Capillary Tubular Reactor

The capillary tubular reactor set-up includes a high pressure syringe pump (ISCO 260D), a tubular piston separator (HIP), a fused silica capillary NMR cell (180 μ m i.d. by 360 μ m o.d., Polymicro Technologies, Inc), and back pressure regulators (Upchurch Scientific). In practice, the resorcinol-D₂O solution was loaded into one side of the piston separator and the other side was filled with water and connected to the syringe pump. The fused silica capillary was bent in a U shape and placed in a 10-mm glass NMR tube so that the bent end did not extend below the bottom edge of the NMR sensitive region along the z-axis. One end of the capillary tube was connected to the solution outlet of the piston separator and the other end of the capillary was connected to the back pressure regulators. When the high pressure syringe pump was operated in a constant flow rate mode, the sample pressure was controlled by the back pressure regulators. Five back pressure regulators (~80 bar each) were used in series so that the sample pressure was maintained between 380 to 400 bar depending on the flow rate.

The detection volume (V) within the NMR sensitive region was estimated from the inner diameter (180 \pm 6 μ m) of the capillary tubular reactor and twice the length of the NMR receiving coil (3.90cm). The volume of the NMR detection region was estimated to be $\sim 9.8 \times 10^{-6}$ ml (0.98

μl). Therefore, the reactor residence time (t_R) may be calculated from the mass flow rate (f) and the solution density (ρ) using equation 1,

$$t_R = V \cdot \rho / f \quad (1)$$

Since the accuracy of the reactor residence time depends on flow rate control and fluid density in the reactor, a system calibration was performed at room temperature and a pressure of 400 bar by collecting and weighing the water eluted from the capillary at specific flow rates over a set time interval. A step profile is assumed for the temperature contour in the reactor region and the density is determined from the Steam Tables⁶. This assumption allows a qualitative determination of the reaction rate under these extreme conditions.

NMR Measurements

All NMR data were obtained on a Varian UnityPlus 300 NMR spectrometer operating at 299.3 and 46.13 MHz for proton and deuterium detection, respectively. A high temperature, high resolution, broad band 10-mm NMR probe (Doty Scientific, Inc.) produces a line width at half-height of 8-10 Hz for proton and 4-8 Hz for deuterium in the resorcinol-D₂O solution in the capillary NMR cell at room temperature. Because of the probe design, there is a region where the tubular reactor temperature is not well controlled. This pre-heated area, before the NMR detection region, could contribute to a overestimation of the deuterated product and a underestimation of the reactant conversion rate. We anticipate solving this problem in future NMR investigations, through redesign of the probe's heated region.

In a typical experiment, the resorcinol-D₂O solution is moving through the capillary high pressure NMR cell⁷ under a constant flow rate at constant temperature and pressure. Concurrent with solution flow, a NMR experiment is running coadding transients until a satisfactory spectrum with an adequate signal to noise ratio is obtained. Since the capillary tubular reactor is an integral part of the NMR capillary cell, a steady state concentration is established in the reactor at constant flow during the experiment. The sample temperature was changed with each flow rate at a constant pressure and the peak integral was used in both the proton and deuterium data analysis.

RESULTS AND DISCUSSION

Proton NMR

The reaction of substituted benzene in basic solutions of D₂O has been discussed by Yao and Evilia.³ The H/D exchange mechanism for resorcinol in pure D₂O is facilitated by the presence of electron-withdrawing groups on the aromatic ring. This activated aromatic ring is deuterated by an electrophilic substitution mechanism, which increases the ease of deuteration under these experimental conditions and eliminates the need of either an acid or base to catalyze the reaction.^{5,8} Resorcinol is an ortho/para director in electrophilic substitution reactions.⁹ Therefore, H/D substitution would be facilitated for the α -hydrogens and not for the β -hydrogen. The α -hydrogen peak area decreased as a function of increasing temperature and reactor residence time. From the H/D substitution reaction rates the pseudo-first order kinetics could be determined for resorcinol under these extreme conditions. The NMR experimental results demonstrate the positional selectivity of the electrophilic substitution during H/D exchange due to the molecular structural information obtained from this technique.

The β -hydrogen in resorcinol can serve as an internal molecular indicator relating to the stability of the molecule to thermolysis reactions under these conditions. Qualitatively, the peak area of the β -hydrogen decreases with increasing reactor residence time, but shows little temperature dependence. Thermolysis of resorcinol at 460°C and 254 bar was reported to produced conversions of ~10%, for residence times of 1 - 7 seconds at 0.01M solution concentration.¹⁰ The NMR results demonstrates the occurrence of a parallel thermolysis reaction of resorcinol under these temperatures and reactor residence times. The thermolysis products could not be identified as they were below the detection limits of the NMR.

Deuterium NMR

At a reaction temperature of 200 °C, the deuterium NMR spectrum shows a new peak with a chemical shift of ~7.2 ppm. The chemical shift difference between this new peak and that of D₂O at 200 °C is ~3.0 ppm, which is the same as the chemical shift difference between the α -hydrogens and water in the ¹H NMR measurement at the same temperature. Therefore, this resonance was assigned to resorcinol deuterated at the α -positions. This qualitative observation demonstrated that H/D exchange did indeed occur for the resorcinol-D₂O solution at 200°C at very long reactor residence times. The intensity of the α -deuterated resorcinol peak increases as a function of temperature and reactor residence time. A pseudo-first order rate constant can be determined from the rate of appearance of the α -deuterium peak and compared with that determined from the ¹H NMR measurements under similar experimental conditions. A β -deuterium peak is not observed under the experimental conditions investigated.

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